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Ab Initio Study of Electronic and Magnetic Structure and Structural Phase Transition of $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{P}_{1-y}\text{Ge}_y$ Alloys

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The paper presents results of the *ab initio* electronic structure calculations performed for the $(\text{Fe}_{0.5}\text{Mn}_{0.5})_2\text{P}_{0.67}\text{Ge}_{0.33}$ alloy, a member of $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{P}_{1-y}\text{Ge}_y$ family of alloys showing a giant magnetocaloric effect. Calculations confirmed the strong relationship between the magnetic state and crystal structure of the alloy. To investigate the isostructural phase transition driven by external magnetic field observed in $(\text{Fe}_{0.9}\text{Mn}_{1.1})\text{P}_{0.8}\text{Ge}_{0.2}$ we utilized the fixed spin moment approach. Total energy analysis confirmed the occurrence of isostructural phase transition.

PACS: 71.20.Be, 75.20.Hr

1. Introduction

Magnetic refrigeration at room temperatures attracts recently high interest due to discovery of new materials showing giant magnetocaloric effect (MCE) [1–3]. The magnetocaloric materials for technological applications must satisfy two criteria: the magnetocaloric cycle must occur at ambient temperatures and with application of magnetic field achievable using permanent magnets. Material satisfying both criteria is the $\text{Gd}_5\text{Ge}_2\text{Si}_2$ alloy reported fourteen years ago [1] and the $\text{MnFeP}_{1-x}\text{As}_x$ alloy discovered in 2002 [3]. Due to high cost of gadolinium and toxicity of As the wide scale application of both materials is questionable. Recently it has been discovered that the replacement of As by Ge or Si atoms does not change the magnetocaloric properties of the material but eliminates the toxicity problem [4]. Liu et al. [5] investigated a particular composition of $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.8}\text{Ge}_{0.2}$ optimal for MCE, with $\text{MCE} \approx 75 \text{ J}/(\text{kg K})$. They reported that the material is single phase both in high temperature (HT) paramagnetic (PM) state and in low temperature (LT) ferromagnetic (FM) state but in between the first-order isostructural transition occurs as a function of temperature or magnetic field. The HT and LT phases are of the same symmetry but have different lattice parameters and internal atomic coordinates [5]. The first-order structural phase transition accompanying the magnetic transition results in an enormous change of the magnetic entropy induced by magnetic field giving the giant magnetocaloric effect.

In the paper we report the preliminary results of our *ab initio* investigations of $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ alloy. The aim of our study was to get more insight into the origin of the simultaneous occurrence of structural (first order) and magnetic (second order) phase transition in $\text{Mn}_x\text{Fe}_{1-x}\text{P}_{1-y}\text{Ge}_y$. With this aim we have performed electronic structure calculations for the $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ alloy in FM (LT) and PM (HT) structures using the ordinary mode of *ab initio* calculations and the fixed-spin-moment (FSM) mode [6] which is a standard technique for searching of magnetically distinct states of studied system.

2. Computational procedure

The electronic structure calculations were performed using the WIEN2k code [7] based on the full-potential linearized augmented plane wave (FP-LAPW) method [8]. The electronic states were partitioned into core states: ([Ne] for Fe, Mn, P and [Ar] for Ge); local orbitals [8] (3s, 3p for Fe, Mn and 3d for Ge) and valence states (3d, 4s for Fe, Mn, 3s, 4p for P and 4s, 4p for Ge). The core states were treated in a fully relativistic manner while for the local orbitals and valence states the scalar-relativistic approximation was applied. The GGA exchange-correlation (XC) potential was used in the form given in [9]. Atomic muffin-tin spheres radii were taken as 1.85 a.u. for Fe, Mn and 2.4 a.u. for P, Ge. The \mathbf{k} -mesh with 63 \mathbf{k} points in the irreducible wedge of the Brillouin zone was used. Other parameters influencing the computational precision [7] were fixed to assure the total energy precision of 1 mRy.

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3. Results and discussion

The $\text{Mn}_x\text{Fe}_{1-x}\text{P}_{1-y}\text{Ge}_y$ alloys crystallize in hexagonal structure of Fe_2P type (space group No. 189). The unit cell of the structure consists of three formula units. Six Fe atoms are located at triple 3f — $(x_1^f, y_1^f, 1/2)$, $(x_2^f, y_2^f, 1/2)$, $(1 - y_2^f, 1 - x_1^f, 1/2)$ and triple 3g — $(x_1^g, y_1^g, 0)$, $(x_2^g, y_2^g, 0)$, $(1 - y_2^g, 1 - x_1^g, 0)$ positions while three P atoms occupy single 1b — $(0, 0, 0)$ and double 2c — $(1/3, 2/3, 1/2)$, $(2/3, 1/3, 1/2)$ sites. In undistorted structure the internal atomic coordinates satisfy relations: $y_1^f = x_2^f = 0$, $x_1^f = y_2^f$, $y_1^g = x_2^g = 0$ and $x_1^g = y_2^g$. The calculations were performed assuming the experimental lattice parameters reported for $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.8}\text{Ge}_{0.2}$ in [5]: for the paramagnetic (PM) structure the parameters measured at 295 K ($a_0 = b_0 = 6.061$ Å, $c_0 = 3.460$ Å) and for ferromagnetic (FM) structure the parameters measured at 200 K ($a_0 = b_0 = 6.161$ Å, $c_0 = 3.338$ Å) were used. The distribution of atoms over lattice sites (3f, 3g, 1b, 2c) was assumed according to the preference established on the basis of

neutron diffraction measurements [5]. We have started our *ab initio* investigations applying the internal atomic coordinates determined experimentally [5] (for FM structure: $x_1^f = y_2^f = 0.2558$ and $x_1^g = y_2^g = 0.5949$; for PM structure: $x_1^f = y_2^f = 0.2527$ and $x_1^g = y_2^g = 0.5916$). Calculations performed for $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ in FM and PM structures with the use of experimental structural data have revealed that substantial forces are exerted on iron (3f-site) and manganese (3g-site) atoms for both spin-polarized and paramagnetic solutions. Before we started the FSM calculations we have performed the relaxation of atomic positions for both structures and considering the ferromagnetic (ferro) and paramagnetic (para) solutions. After relaxation coordinates of 1b and 2c sites did not change. Replacement of smaller P atom by a greater Ge one have led to displacement of neighboring Fe and Mn atoms. Directions and magnitudes of displacements depend on type of structure (PM, FM) and on the magnetic state (para, ferro). The relaxed internal parameters x_i^α and y_i^α ($i = 1, 2$ and $\alpha = f, g$) are collected in Table.

TABLE

Parameters of the internal atomic coordinates obtained after relaxation of atoms to equilibrium positions.

| Structure | | x_1^f | y_1^f | x_2^f | y_2^f | x_1^g | y_1^g | x_2^g | y_2^g |
|-----------|-------|---------|---------|---------|---------|---------|---------|---------|---------|
| PM | ferro | 0.2407 | 0.9858 | 0.0142 | 0.2549 | 0.5852 | 0.9830 | 0.0170 | 0.6022 |
| | para | 0.2471 | 0.9960 | 0.0040 | 0.2511 | 0.5773 | 0.9566 | 0.0434 | 0.6207 |
| FM | ferro | 0.2456 | 0.9878 | 0.0122 | 0.2578 | 0.5914 | 0.9845 | 0.0155 | 0.6070 |
| | para | 0.2477 | 0.0019 | 0.9981 | 0.2458 | 0.5695 | 0.9431 | 0.0569 | 0.6264 |

The relaxed internal parameters y_i^α do not satisfy relations characteristic for undistorted structure of Fe_2P -type and deviate noticeably from those determined experimentally [5] for PM structure in paramagnetic state and for FM structure in ferromagnetic state. The results of relaxation collected in Table clearly show that atomic positions in 3f and 3g sublattices in both structures (PM, FM) depend on the magnetic state (para or ferro). The correlation between atomic positions and magnetic state may be related to the isostructural phase transition observed in $\text{Mn}_{1.1}\text{Fe}_{0.9}\text{P}_{0.8}\text{Ge}_{0.2}$ at temperatures near T_C . In the relaxed structures we have obtained the local magnetic moments for Mn and Fe equal: $\mu_{\text{Fe}} = 1.45 \mu_B$, $\mu_{\text{Mn}} = 2.79 \mu_B$ in FM structure; $\mu_{\text{Fe}} = 1.36 \mu_B$, $\mu_{\text{Mn}} = 2.76 \mu_B$ in PM structure (experimental values are: $\mu_{\text{Fe}} \approx 1 \mu_B$, $\mu_{\text{Mn}} \approx 3 \mu_B$). Induced magnetic moments of P and Ge atoms are of order of $0.1 \mu_B$.

Figure 1 shows spin-resolved atomic partial densities of states (DOS) in $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ calculated for FM and PM lattice structures. The two isolated subbands located below the main complex of valence band (VB) are formed of P 3s states (at higher binding energy (BE)) and Ge 4s states (at lower BE). The main complex of VB is composed of two clearly separated parts.

At the lower part of VB the P 3p and Ge 4p states hybridized with 3d states of Fe and Mn form the subband of 4 eV width. Strong hybridization of Ge 4p states may indicate covalent bonding of Ge with surrounding atoms (Fe, Mn, P). Upper part of the VB is constructed essentially of the TM 3d (TM = Fe, Mn) states. The band structures obtained for PM and FM structures differ only near the Fermi level in the minority spin channel. Deep valley, present at the Fermi level (ε_F) in the minority spin DOS of FM structure, in the PM structure is filled by antibonding d-states of Fe. The shift of the antibonding 3d-states of Fe below ε_F affects the bonding properties of the FM and PM structures. Our calculations have shown that after transition to the Pauli paramagnetic state the minority spin antibonding 3d states will shift to higher BE but remain about ε_F while the majority-spin 3d states will shift above ε_F . Both shifts will change the bonding of TM atoms with surrounding atoms which may result in isostructural reconstruction of unit cell upon changes of magnetization.

To verify this hypothesis we performed the FSM calculations. In the standard spin-polarized calculations the number of electrons in both spin channels are determined self-consistently with the constraint that $n_\uparrow + n_\downarrow$ is equal to the total number of electrons in the system. In the

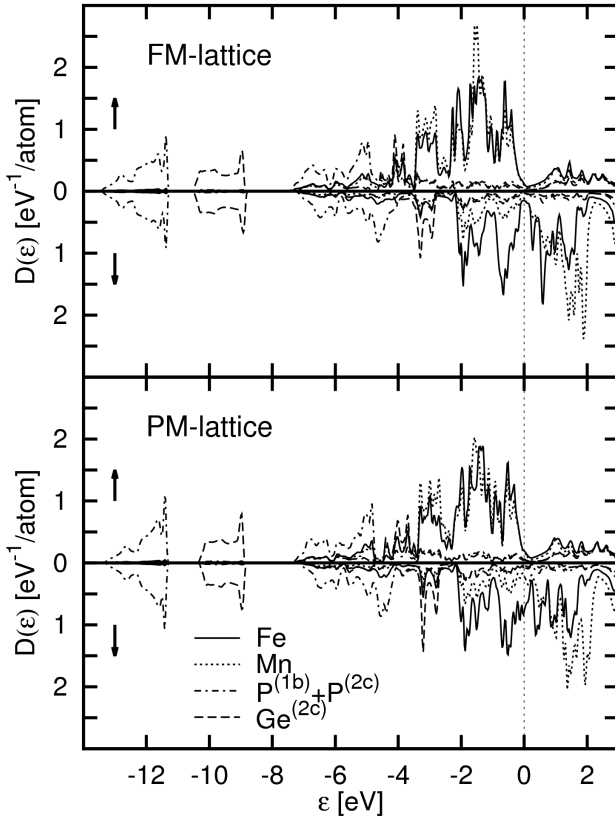


Fig. 1. Spin-resolved partial atomic density of states calculated for $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ alloy in FM and PM types of lattice structures. Energy scale zero shifted to the Fermi energy.

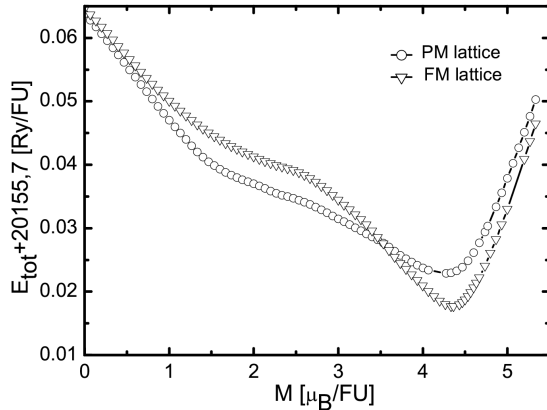


Fig. 2. FSM results for internal energy as a function of total spin moment (M) in $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ alloy calculated for FM and PM lattice structures.

FSM mode of *ab initio* calculations an additional constraint is imposed on the total magnetic moment, i.e.

$n_{\uparrow} - n_{\downarrow}$ must gain a specified value. In terms of the Stoner model, the FSM mode of *ab initio* calculations can be considered as simulations of an effect of static external magnetic field on paramagnetic material. The FSM calculations make possible determination and analysis of the internal energy and local magnetic order as a function of the total magnetic moment.

Figure 2 presents the magnetization dependence of the total internal energy of $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ alloy calculated for FM and PM lattice structures using the FSM method. FSM calculations have shown that at the $M_{\text{tot}} \approx 3.5 \mu_B$ the $\text{Mn}_{1.0}\text{Fe}_{1.0}\text{P}_{0.67}\text{Ge}_{0.33}$ alloy may undergo the structural phase transition from FM-type at higher to PM-type at lower values of total magnetic moments. Below critical value of magnetic moment the E_{tot} vs. M_{tot} curves for both structures have a plateau indicating possibility of metastable magnetic order of FM and PM structures in this range of total magnetic moment. The FSM calculations have shown that the reduction of the total magnetic moment is realized by the reduction of iron local magnetic moment. Below $M_{\text{tot}} \approx 3.5 \mu_B$ the iron magnetic moment polarizes oppositely to that of manganese and its magnitude grows.

Acknowledgments

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